PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
A02-40015/TK		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/NL02/00119	22/02/2002	22/02/2001
International Patent Classification (IPC) or national classification and IPC C07C2/32		
Applicant STICHTING DUTCH POLYMER INSTITUTE et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 6 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
18/09/2002	21.05.2003
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Goetz, G Telephone No. +49 89 2399 8105

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL02/00119

I. Basis f the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:
Description, pages:

1-4,6-20	as originally filed			
5,5a	as received on	10/03/2003	with letter of	10/03/2003

Claims, No.:

1-20	as received on	10/03/2003	with letter of	10/03/2003

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   - ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
   - ☐ the language of publication of the international application (under Rule 48.3(b)).
   - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   - ☐ contained in the international application in written form.
   - ☐ filed together with the international application in computer readable form.
   - ☐ furnished subsequently to this Authority in written form.
   - ☐ furnished subsequently to this Authority in computer readable form.
   - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
   - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   - ☐ the description, pages:
   - ☐ the claims, Nos.:
   - ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1,3-14
	No:	Claims	15-20
Inventive step (IS)	Yes:	Claims	1,3-14
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1,3-20
	No:	Claims	

2. Citations and explanations
   see separate sheet

Re It m V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

D1: EP-A-0608447
D2: Journal Of Organometallic Chemistry, Elsevier-sequoia S.a. Lausanne, Ch (1999), 592, 84-94
D3: WO-A-9425416

1. Present claim 2 as well as the amendment on page 5 does not meet the requirements of Article 19(2) PCT: there is no basis to be found in the application as filed for a "pressure from 0,2 to 14 MPa".

2. The catalyst system used in the trimerization process is known from D2 (as already acknowledged from the applicant in the description).
A catalyst is not rendered novel by the mere fact that this catalyst may be used in a novel process.
Present claims 15 to 20 are thus not novel over the prior art disclosed in D2 (PCT Article 33.2).

3 The claimed trimerization process according to claims 1 and 14 is not disclosed in any of the available prior art documents D1 to D3).
The subject matter of present claims 1, 3 to 14 is thus considered to be novel over said prior art (PCT Article 33.2).

4. There is no hint to be found in any of the prior art documents that the catalyst system known from D2 could be used in the trimerization of olefinic compounds according to present claims 1, 3 14.
In particular the disclosure of D2 leads away from such a use of the known catalyst system since it is indicated in D2 (see page 89 left column) that the catalyst system used in D2 leads to polymer products.
The subject matter of present claims 1, 3 to 14 is thus regarded to be based on an inventive step (PCT Article 33.3)

3. The industrial applicability is given for all claims examined (Article 33.4 PCT)

Printed:16-05-2003 DESCPAMD 02700895-NL-020011

EPO - DG 1
10. 03. 2003

that any activator can be used provided that it is abl to generate a cationic transition metal species with a non-coordinating anion (43). The term "non-coordinating anion" is meant to indicate the anionic part or derivative of the activator, which not or only weakly coordinates to the cationic form of the present catalyst system.

Preferably the activator is methylalumoxane (also known as MAO). The molar ratio of Ti:Al is expediently from 1:100 to 1:1000.

The present catalyst system can further also comprise a scavenger. Examples of a scavenger are i-Bu_3Al and $(i\text{-}Bu_2Al)_2O$. A scavenger is normally used to scavenge impurities from a polymerisation medium to obtain a high productivity.

The invention further relates to a process to trimerize olefinic compounds which comprises carrying out said trimerisation in the presence of a catalyst system, as described above, under trimerisation conditions. Such a trimerisation als comprises co-trimerisation according to the definition given before.

The olefin to be trimerized is preferably selected from C_2-C_{20} olefins or mixtures of two or more of these olefins. The preferred olefins are ethylene and 1-butene, more preferably ethylene.

The temperature is preferably in the range of from 20-150°C, at a pressure which is commonly in the range from 0,2 to 14 MPa, preferably in the range of from 1,5 to 3 MPa.

The invention will further be explained in the following examples.

Experimental section

General considerations

All experiments were performed under a nitrogen atmosphere using standard Schlenk and glovebox techniques. Deuterated solvents (Aldrich, Acros) were dried over Na/K alloy and vacuum transferred before use. Cyclooctane (Aldrich, used as internal standard) was distilled from Na prior to use. Toluene (Aldrich, anhydrous, 99,8%) was passed over columns of Al_2O_3 (Fluka), BASF R3-11 supported Cu oxygen and molecular sieves (Aldrich, 4Å). Diethyl ether and THF (Aldrich) were dried over Al_2O_3 (Fluka) and the other solvents (Aldrich) were dried over molecular si ves (Aldrich, 4Å). Ethene

10-03-2003

Printed:16-05-2003 DESCPAMD 02700895-NL_020011.9

(AGA polymer grade) was passed over BASF R3-11 supported Cu oxygen scav nger and molecular sieves (Aldrich, 4Å).

The compounds 6,6-p ntamethyl nefulvene, $C_5H_5CH_2Ph$, $(C_5H_4C(=CH_2)Ph)Li$, $(C_5H_4CMe_2Ph)TiCl_3$ (th catalyst us d in

10-03-2003

NEW CLAIMS

(43) 1. A process for the selective trim rization of olefinic compounds under trimerization conditions in the presence of a catalyst system, characterized in that said process is effected by using a catalyst system which comprises

A) a cyclopentadienyl titanium complex of formula

$(Cp\text{-}B(R)_nAr)TiR^1_3$

wherein

Cp is a cyclopentadienyl type ligand, optionally being substituted,

B is a bridging group, based on a single atom selected from the groups 13 to 16 inclusive of the Periodic System,

Ar is a aromatic group, optionally substituted,

R is, independently, hydrogen, or a hydrocarbon residue, optionally being substituted and optionally containing heteroatoms, or groups R and B are joined together to form a ring,

n is an integer equal to the (valency of B minus 2), and

R^1 is a monò-anionic group, and

B) an activator,

and wherein said olefinic compounds are selected from C_2-C_{20} olefines and mixtures of two or more of these olefins.

2. A process according to claim 1, wherein said process is effected at a temperature from 20-150°C, at a pressure from 0,2 to 14 MPa, preferably 1,5 to 3 MPa.

3. A process according to any of the claims 1 or 2, wherein the single atom forming the basis of group B is selected from B, C, N, O, Si, P and S.

4. A process according to any of the claims 1 to 3 wherein the single atom forming the basis of said group B consists of carbon or silicon,

Ar is phenyl, optionally substituted or being part of a larger

aromatic ntity,

R^1 is a halogen atom, or mono-anionic hydrocarbon r sidu optionally containing heteroatoms, and

n is 2, then R is a mono-anionic hydrocarbon residue, optionally containing heteroatoms, or

n is 1, then R is a di-anionic hydrocarbon residue, optionally containing heteroatoms.

5. A process according to any of the claims 1 to 4, wherein Cp is a cyclopentadienyl type ligand being substituted, besides said B-(R)n group, with 1 to 8 groups of formula -YR2R3R4 in which Y is C or Si and R2, R3 and R4 are, independently, H, halogen, lower alkyl, aryl, lower-alkyl-aryl, aryl-lower alkyl residue, wherein said alkyl and aryl are independently substituted or not with one or more lower alkyl residues, said alkyl and aryl residues being independently provided or not with at least one heteroatom, selected from halogen, nitrogen, oxygen, sulfur and phosphor.

6. A process according to any of the claims 1 to 5, wherein said lower alkyl residues, being the same or different to each other, are linear or branched C_1-C_5 alkyl residues, more specifically methyl.

7. A process according to any of the claims 1 to 6, wherein said aryl group in the alkylaryl or arylalkyl residue is a phenyl group.

8. A process according to any of the claims 4 or 5, wherein said halogen is fluorine or chlorine.

9. A process according to any of the claims 1 to 8, wherein Ar is a phenyl group, substituted or not at the meta-or para-position,

B is based on a carbon atom,

n is 2, th n groups R are, independently, methyl, or ethyl; or

n is 1, then group R is $=CH_2$, or forms when R is C_4H_8 or C_5H_{10}

tog ther with group B a dianionic cyclic group

Cp is C_5H_4 or $C_5H_3(SiMe_3)$, or $C_5H_3(CMe_2Ph)$, and

R^1 is chlorin , methyl, or benzyl.

10. A process according to any of the claims 1 to 9, wherein said titanium complex is supported on a carrier.

11. A process according to any of the claims 1 to 10, wherein said activator is methylalumoxane, a salt of a non-coordinating anion, or a Lewis acid capable of abstracting an anion from said transition metal complex.

12. A process according to claim 11 wherein the activator is methylalumoxane and the molar ratio of Ti:Al is from 1:100 to 1:1000.

13. A process according to any of the claims 1 to 12, wherein said catalyst system further comprises a scavenger.

14. A process according to claim 13, wherein said scavenger is selected from *i*-Bu_3Al and $(i\text{-}Bu_2Al)_2O$.

15. A catalyst system for the selective trimerization of olefins, characterized in that said catalyst system comprises

A) a half-sandwich substituted cyclopentadienyl titanium complex of formula

$(Cp\text{-}B(R)_nAr)TiR^1_3$

wherein

Cp is a cyclopentadienyl type ligand, optinally substituted,

B is a bridging group, based on a single atom selected from the groups 13 to 16 inclusive of the Periodic System,

Ar is a aromatic group, optionally substituted,

R is, independently, hydrogen, or a hydrocarbon residue, optionally being substituted and optionally containing heteroatoms, or groups R and B are joined together to form a ring,

n is an integer equal to the (valency of B minus 2), and

R^1 is a mono-anionic group, and

b) an activator.

16. A catalyst system according to claim 15, wherein the single atom forming the basis of group B is selected from B, C, N, O, Si, P and S.

17. A catalyst system according to any of the claims 15 or 16 wherein the single atom forming the basis of said group B consists of carbon or silicon,

Ar is phenyl, optionally substituted or being part of a larger aromatic entity,

R^1 is a halogen atom, or mono-anionic hydrocarbon residue optionally containing heteroatoms, and

n is 2, then R is a mono-anionic hydrocarbon residue, optionally containing heteroatoms, or

n is 1, then R is a di-anionic hydrocarbon residue, optionally containing heteroatoms.

18. A catalyst system according to any of the claims 15 to 17, wherein Cp is a cyclopentadienyl type ligand being substituted, besides said B-(R)n group, with 1 to 8 groups of formula -YR2R3R4 in which Y is C or Si and R2, R3 and R4 are, independently, H, halogen, lower alkyl, aryl, lower-alkyl-aryl, aryl-lower alkyl residue, wherein said alkyl and aryl are independently substituted or not with one or more lower alkyl residues, said alkyl and aryl residues being independently provided or not with at least one heteroatom, selected from halogen, nitrogen, oxygen, sulfur and phosphor.

19. A catalyst system according to any of the claims 15 to 18, wherein said lower alkyl residues, being the same or different to each other, are linear or branched C_1-C_5 alkyl residues, more specifically methyl.

20. A catalyst system according to any of the claims 15 to 19,

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
A02-40015/TK		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/NL 02/ 00119	22/02/2002	22/02/2001
Applicant		
STICHTING DUTCH POLYMER INSTITUTE		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. _____

   [ ] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [X] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 02/00119

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C2/32 B01J31/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 608 447 A (PHILLIPS PETROLEUM CO) 3 August 1994 (1994-08-03) cited in the application claims 20-24 ---	14,15
X	SASSMANNSHAUSEN J ET AL: "HALF-SANDWICH COMPLEXES OF TITANIUM AND ZIRCONIUM WITH PENDANT PHENYL SUBSTITUENTS. THE INFLUENCE OF ANSA-ARYL COORDINATION ON THEPOLYMERISATION ACTIVITY OF HALF-SANDWICH CATALYSTS" JOURNAL OF ORGANOMETALLIC CHEMISTRY, ELSEVIER-SEQUOIA S.A. LAUSANNE, CH, vol. 592, 1999, pages 84-94, XP001033815 ISSN: 0022-328X cited in the application table 1 --- -/--	1-13

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 April 2002	29/04/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Goetz, G

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 02/00119

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 25416 A (SHELL INT RESEARCH) 10 November 1994 (1994-11-10) page 2, line 14 -page 3, line 4	14,15

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/NL 02/00119

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0608447 A	03-08-1994	AU	650808 A1	30-06-1994
		CA	2087578 A1	20-07-1994
		CZ	9300088 A3	17-08-1994
		JP	3188335 B2	16-07-2001
		JP	6239920 A	30-08-1994
		NO	930340 A	02-08-1994
		EP	0608447 A1	03-08-1994
		AT	207084 T	15-11-2001
		DE	69330943 D1	22-11-2001
		DE	69330943 T2	11-04-2002
		DK	608447 T3	11-02-2002
		ES	2161699 T3	16-12-2001
WO 9425416 A	10-11-1994	AU	683060 B2	30-10-1997
		AU	6650394 A	21-11-1994
		BR	9406460 A	30-01-1996
		CA	2161664 A1	10-11-1994
		CN	1121704 A ,B	01-05-1996
		CZ	9502826 A3	15-05-1996
		DE	69405222 D1	02-10-1997
		DE	69405222 T2	02-01-1998
		DK	696263 T3	29-09-1997
		WO	9425416 A1	10-11-1994
		EP	0696263 A1	14-02-1996
		FI	955104 A	26-10-1995
		JP	8509518 T	08-10-1996
		NO	954292 A	26-10-1995